

Calculation of g and g' for iron and nickel*

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The spectroscopic splitting factor g and magnetomechanical ratio g' are studied in reference to ferromagnetic metals within the framework of the tight-binding approximation. General formulas are obtained which include overlap effects in the calculation of the average of the orbital angular momentum as well as terms resulting from the nonperiodic nature of L_z , plus spin-orbit and other relativistic correction terms. Wave functions obtained from recent band calculations are used to obtain numerical results for iron ($g = 2.05$, $g' = 1.95$) and nickel ($g = 2.14$, $g' = 1.87$).

I. INTRODUCTION

There have been a few attempts to calculate the magnetomechanical ratio g' and the spectroscopic splitting factor g for ferromagnetic metals.¹⁻⁴ The magnetomechanical ratio is defined as the ratio of the magnetic moment to the total angular momentum, while the spectroscopic splitting factor is the ratio of magnetic moment to spin.⁵ More precisely, we must consider the components of these vector quantities in the direction of the magnetization (here called the z direction), so that (mks units are used throughout)

$$\frac{eg}{2m} = \frac{\langle M_z \rangle}{\langle S_z \rangle}, \quad \frac{eg'}{2m} = \frac{\langle M_z \rangle}{\langle L_z + S_z \rangle}. \quad (1.1)$$

The angular brackets indicate ground-state averages. The quantities can also be defined for a single electron, in which case we refer to $g_n(\vec{k})$ (n is the band index and \vec{k} is the wave vector of an electron state). More generally, we can define a g tensor, relating the entire magnetization vector to the spin vector. However, for a cubic crystal, the only component of L and S which has a nonzero average over occupied states is that in the direction of magnetization.

We define

$$2\epsilon = \langle L_z \rangle / \langle S_z \rangle. \quad (1.2)$$

It follows from (1.1) that

$$g = (1 + 2\epsilon)g'. \quad (1.3)$$

To the extent that corrections due to spin-orbit coupling and other relativistic effects can be neglected,

$$\langle M_z \rangle = (e/2m)(\langle L_z \rangle + 2\langle S_z \rangle). \quad (1.4)$$

In this case,⁶

$$g^{-1} + g'^{-1} = 1. \quad (1.5)$$

Since ϵ is found to be small, it is a good approximation to neglect terms of second order in ϵ , so

that we have^{5,6}

$$g - 2 = 2 - g' = 2\epsilon. \quad (1.6)$$

The available experimental data indicate that Eq. (1.6) is satisfied within uncertainties of (10–15)%.⁷⁻⁹

Previous calculations of the g factor in ferromagnetic transition metals have been based on highly simplified forms of the tight-binding method or on related interpolation schemes.¹⁻⁴ The present work was motivated by the availability of wave functions from a detailed band calculation including spin-orbit coupling, which should make possible a more accurate calculation of g and g' . Furthermore, it seemed desirable to present a full expression for g within the framework of the tight-binding method, as this has not been done previously and at least to estimate all the terms which arise. Our conclusion is that the terms omitted in previous analyses are in fact, reasonably negligible, of the order of 5% or less of the dominant term.

The plan of this paper is as follows. Section II contains a derivation of the formal expressions from which g and g' are computed. The argument is based on the Dirac equation and includes some discussion of the problems of gauge and phase which have been quite troublesome in previous work. Section III contains a brief discussion of the computational techniques, the results, and a comparison with experiment.

II. THEORY

The essential problem in a calculation of the g or g' factors is to determine the magnetic moment. We define the magnetic moment in the following way. In the absence of an external magnetic field, the system is described by a Hamiltonian H_0 , say. If there is an applied field \vec{B} , the Hamiltonian can be written after some manipulation as

$$H = H_0 + \vec{M} \cdot \vec{B} + O(B^2). \quad (2.1)$$

The notation $O(B^2)$ indicates terms of second order in the external field. The operator \vec{M} is independent of time and magnetic field. The field-independent portion of the magnetization at $T=0^\circ\text{K}$ can be determined as the expectation value of the operator \vec{M} , calculated with wave functions which are eigenfunctions of H_0 . This is all that is of interest in our discussion of g' in ferromagnets. We will call \vec{M} the zero-order magnetic-moment operator. In nonferromagnetic systems, the expectation value of \vec{M} will vanish, if calculated with wave functions for $B=0$, and the magnetization is ultimately found to be proportional to B . Even in such cases \vec{M} may still be used to calculate the explicitly spin dependent contribution to the energy of the system in a magnetic field, and thus, the g factor. Our first task is to obtain an expression for \vec{M} . We will consider only a single particle picture at $T=0^\circ\text{K}$. The answer is simple when relativistic corrections can be neglected. It is then

$$\vec{M} = e(\vec{L} + 2\vec{S})/2m. \quad (2.2)$$

Complications arise when relativistic effects are included.

The theory underlying the calculation of g or g' factors has been both complicated and controversial.¹⁰⁻¹⁵ We will therefore begin with a derivation of the effective interaction between an electron and an external magnetic field starting from the Dirac equation. This is done so that the origin of the various terms included in \vec{M} will be clear. The Dirac equation for a single electron (charge $-e$) is

$$\left(i\hbar \frac{\partial}{\partial t} + e\Phi\right)\Psi = (c\vec{\alpha} \cdot \vec{P} + \beta mc^2)\Psi, \quad (2.3)$$

in which Φ is a fixed potential (including but not restricted to the periodic potential of the crystal), and \vec{P} is given by

$$\vec{P} = \vec{p} + e\vec{A}, \quad (2.4)$$

where \vec{p} is the ordinary momentum [$\vec{p} = (\hbar/i)\nabla$] and \vec{A} is the vector potential of the external field.

It is assumed that the external potential Φ and the magnetic field \vec{B} are time independent as is the case for both the symmetric gauge and for the Jones-Zener¹⁶ gauge used by de Graaf and Overhauser.¹⁴ The standard procedure¹⁷ for reducing the Dirac equation for the four component spinor Ψ to the Pauli equation for a two component spinor ψ leads to

$$\begin{aligned} i\hbar \frac{\partial \psi}{\partial t} = & \left(\frac{(\vec{P} \cdot \sigma)^2}{2m} - e\Phi + mc^2 \right) \psi \\ & - \frac{1}{4m^2c^2} \left(\frac{(P \cdot \sigma)^4}{2m} - \hbar \sigma \cdot (e\vec{\mathcal{E}} \times \vec{P}) - \frac{\hbar^2 e}{2} \nabla \cdot \vec{\mathcal{E}} \right) \psi. \end{aligned} \quad (2.5)$$

The last term in (25) is obtained by using the relation

$$\vec{P} \cdot \vec{\mathcal{E}} - \vec{\mathcal{E}} \cdot \vec{P} = (\hbar/i)\nabla \cdot \mathcal{E},$$

in which \mathcal{E} is the electric field

$$\vec{\mathcal{E}} = -\nabla\Phi - \frac{\partial \vec{A}}{\partial t}. \quad (2.6)$$

For the purpose of investigating the g factor, we may drop all terms which are higher than first order in the magnetic field. It is also assumed at this point that \vec{B} is uniform, and $\nabla \cdot \vec{A} = 0$:

$$\begin{aligned} i\hbar \frac{\partial \psi}{\partial t} = & \left[\frac{p^2}{2m} + \frac{e}{m} \left(1 - \frac{p^2}{2m^2c^2} \right) (\vec{A} \cdot \vec{p}) - e\Phi + mc^2 \right. \\ & - \frac{p^4}{8m^3c^2} + \frac{\hbar \vec{\sigma}}{4m^2c^2} \cdot (e\vec{\mathcal{E}} \times \vec{p}) \\ & + \frac{\hbar e^2 \vec{\sigma} \cdot (\vec{\mathcal{E}} \times \vec{A})}{4m^2c^2} + \left. \frac{\hbar^2 e}{8m^2c^2} \nabla \cdot \vec{\mathcal{E}} \right] \psi \\ & + \frac{e\hbar}{2m} \left(1 - \frac{p^2}{2m^2c^2} \right) \vec{\sigma} \cdot \vec{B} \psi. \end{aligned} \quad (2.7)$$

The factor multiplying $\vec{\sigma} \cdot \vec{B}$ contains a relativistic correction discussed by Overhauser and de Graaf.¹³ A similar term multiplies $\vec{A} \cdot \vec{p}$.

In order to proceed, we have to choose an expression for the vector potential. The usual choice is the symmetric gauge

$$\vec{A} = \frac{1}{2}\vec{B} \times \vec{r} \quad (2.8)$$

de Graaf and Overhauser¹⁴ criticize this choice of gauge and recommend the Jones-Zener gauge¹⁶

$$\vec{A} = \frac{1}{2}\vec{B} \times (\vec{r} - \vec{v}_g t) \quad (2.9a)$$

plus a scalar potential Φ' (in addition to the crystal potential)

$$\Phi' = \frac{1}{2}(\vec{B} \times \vec{v}_g) \cdot \vec{r}, \quad (2.9b)$$

in which \vec{v}_g is the group velocity of a wave packet

$$\vec{v}_g = \hbar^{-1} \nabla_{\mathbf{k}} E(\vec{k}).$$

Use of the symmetric gauge leads to the difficulty that the expression obtained for the expectation value of the operator \vec{M} in (2.1) will be altered by a change in phase of the Bloch functions. The Jones-Zener gauge as employed by de Graaf and Overhauser¹⁴ produces a time-dependent Hamiltonian. The average energy of a state in this case cannot be found by simply setting $t=0$ in the Hamiltonian and calculating the expectation value with the usual Bloch function. Moore points out that an additional term must be added to the Hamiltonian in order that the average energy can be calculated in the usual way.¹⁵ This term, which is proportional to the time derivative of the function inducing the gauge transformation has the effect of can-

celling the contribution of the potential Φ' [Eq. (2.9b)].

We will adopt a procedure which leads to the same result as that of Moore. The origin of the phase dependence of the expectation value of \vec{M} is that the operator \vec{r} is not a bounded operator on the space of Bloch functions. Its matrix elements are highly singular. Suppose we consider the vector potential relevant to a particular Bloch state $\psi_n(\vec{k}, \vec{r})$. We formally subtract from the coordinate \vec{r} in (2.8) its average value in this state $\langle \vec{r} \rangle$ ignoring the singularity of this object

$$\vec{A} = \frac{1}{2} \vec{B} \times (\vec{r} - \langle \vec{r} \rangle). \quad (2.9c)$$

This is, in fact, the choice of Jones and Zener,¹⁶ except that we will consider $\langle \vec{r} \rangle$ to be independent of time, as is correct for a single Bloch state, while for a wave packet $\langle \vec{r} \rangle = \vec{v}_g t$. Note that the average of the coordinate for a Bloch state does not vanish except for some points of high symmetry in the Brillouin zone. In our case no additional scalar potential need be added to the Hamiltonian. We find results which agree with those of Moore and are independent of the phase of the Bloch functions.

We substitute (2.9c) into (2.7). The result can be expressed as

$$i\hbar \frac{\partial \psi}{\partial t} = (H_0 + \vec{M} \cdot \vec{B}) \psi \quad (2.10)$$

in agreement with (2.1). H_0 and \vec{M} are independent of \vec{B} and time, and

$$\vec{M} = (e/2m)[(\vec{r} - \langle \vec{r} \rangle) \times \vec{\pi} + (2 - p^2/m^2c^2)\vec{s}]. \quad (2.11)$$

The notation of (2.11) includes $\vec{s} = \frac{1}{2}\hbar\vec{\sigma}$, and

$$\vec{\pi} = (1 - p^2/2m^2c^2)\vec{p} + (1/2mc^2)\vec{s} \times e\vec{\mathcal{E}}. \quad (2.12)$$

Equations (2.11) and (2.12) describe the first-order interaction of an electron in a definite Bloch state with a magnetic field, including the leading relativistic corrections.

The present work is concerned with the calculation of the average value of the operator \vec{M} , using the wave functions obtained in previous calculations of energy bands in iron¹⁸ and nickel.¹⁹ These calculations were made using a form of the linear-combination-of-atomic-orbitals (LCAO) or tight-binding method. Therefore, we develop expressions for \vec{M} based on an expansion of the wave function in a basis of localized orbitals which are not necessarily orthogonal. This contrasts with procedures employed in studies of the g factor in alkali metals for example where other wave-function expansions are frequently employed. In addition, the band calculations mentioned above included spin-orbit coupling, so it is not necessary for us to perform a perturbation calculation to allow for the modification of the band wave functions

by spin-orbit effects. It is already there.

The calculation of the g factor still contains technical difficulties. These arise from the fact, mentioned previously, that the coordinate operator \vec{r} in (2.11) is not a bounded operator. Its matrix elements involve derivatives of δ functions, and must be handled with caution. In order to facilitate this, we shall at first smear the Bloch functions over a range of wave vectors. Let $\psi_n(\vec{k}, \vec{r})$ be a two-component spinor Bloch wave function for a state of wave vector \vec{k} in band n . We introduce a function $\Psi_n(\vec{k}, \vec{r})$ through

$$\Psi_n(\vec{k}, \vec{r}) = \int f(\vec{k} - \vec{k}') \psi_n(\vec{k}', \vec{r}) d^3k', \quad (2.13)$$

where $f(\vec{k} - \vec{k}')$ is a sharply peaked real time-independent function which is normalized so that

$$\int_{-\infty}^{\infty} f^2(\vec{k} - \vec{k}') d^3k' = 1. \quad (2.14)$$

To be specific, we may consider f to be a Gaussian, although an explicit form is not required. At a suitable point in the calculation, we allow f^2 to approach a δ function. It may be objected that this is a use of wave packets which requires consideration of time dependence. However, if this is admitted, the use of the procedure of Moore¹⁵ leads to the same results as we obtain below.

We shall calculate the expectation value of \vec{M} with the smeared function Ψ_n . A general formal expression is given below

$$\begin{aligned} M_n(\vec{k}) = \langle n\vec{k} | \vec{M} | n\vec{k} \rangle = \frac{e}{2m} \left(2\vec{S}_n(\vec{k}) + \vec{L}_n(\vec{k}) + \frac{1}{2m^2c^2} \vec{D}_n(\vec{k}) \right. \\ \left. - \frac{1}{m^2c^2} \vec{Q}_n^{(1)}(\vec{k}) - \frac{1}{2m^2c^2} \vec{Q}_n^{(2)}(\vec{k}) \right), \end{aligned} \quad (2.15)$$

where

$$\vec{S}_n(\vec{k}) = \langle n\vec{k} | \vec{s} | n\vec{k} \rangle, \quad (2.16)$$

$$\vec{L}_n(\vec{k}) = \langle n\vec{k} | \vec{r} \times \vec{p} | n\vec{k} \rangle - \langle n\vec{k} | \vec{r} | n\vec{k} \rangle \times \langle n\vec{k} | \vec{p} | n\vec{k} \rangle, \quad (2.17)$$

$$\begin{aligned} \vec{D}_n(\vec{k}) = \langle n\vec{k} | \vec{r} \times (\vec{s} \times e\vec{\mathcal{E}}) | n\vec{k} \rangle \\ - \langle n\vec{k} | \vec{r} | n\vec{k} \rangle \times \langle n\vec{k} | (\vec{s} \times e\vec{\mathcal{E}}) | n\vec{k} \rangle, \end{aligned} \quad (2.18)$$

$$\vec{Q}_n^{(1)}(\vec{k}) = \langle n\vec{k} | p^2 \vec{s} | n\vec{k} \rangle, \quad (2.19)$$

$$\begin{aligned} \vec{Q}_n^{(2)}(\vec{k}) = \langle n\vec{k} | \vec{r} \times p^2 \vec{p} | n\vec{k} \rangle - \langle n\vec{k} | \vec{r} | n\vec{k} \rangle \times \langle n\vec{k} | p^2 \vec{p} | n\vec{k} \rangle. \end{aligned} \quad (2.20)$$

The angular brackets indicate matrix elements involving states Ψ

$$\langle n\vec{k} | \mathcal{O} | n\vec{k} \rangle = \int \Psi_n^*(\vec{k}, \vec{r}) \mathcal{O} \Psi_n(\vec{k}, \vec{r}) d^3r.$$

The integrations in (2.15)–(2.20) include summations over spin components. We shall refer to the

direction of the magnetic field \vec{B} as z , thus only the z components of the vectors \vec{s} , \vec{L} , \vec{D} , $\vec{Q}^{(1)}$, and $\vec{Q}^{(2)}$ are required. After the expressions have been evaluated and the limit $f^2 - \delta$ has been employed, the result is to be summed over all occupied states.

Aside from the obvious term \vec{S}_n , which gives the average spin, the term \vec{L}_n is expected to give the most important contribution to g (or g') in a d band metal. This is also the term whose analysis causes the most difficulty. Let us consider the first term on the right-hand side of (2.17), which we shall denote $\vec{L}_n^{(1)}(\vec{k})$. We will examine this term in detail. The Bloch function $\psi_n(\vec{k}, \vec{r})$ is expressed as

$$\psi_n(\vec{k}, \vec{r}) = \left(\frac{\Omega}{8\pi^3} \right)^{1/2} \sum_{\mu} e^{i\vec{k} \cdot \vec{R}_{\mu}} \phi_n(\vec{k}, \vec{r} - \vec{R}_{\mu}), \quad (2.21)$$

in which Ω is the volume of the unit cell, \vec{R}_{μ} is a direct lattice vector, and

$$\phi_n(\vec{k}, \vec{r} - \vec{R}_{\mu}) = \sum_i c_{ni}(\vec{k}) u_i(\vec{r} - \vec{R}_{\mu}). \quad (2.22)$$

The u_i are the basis of localized orbitals, and the coefficients $c_{ni}(\vec{k})$ are determined from the eigenvectors of the Hamiltonian and overlap matrices in the energy-band calculation. In the specific calculations referred to above, the u_i are Gaussian-type orbitals. Equation (2.21) is substituted into (2.17). After some straightforward algebra, we obtain

$$\begin{aligned} \vec{L}_n^{(1)}(\vec{k}) = \frac{\Omega}{2(2\pi)^3} \int d^3s \int d^3q f(\vec{k} - \vec{s}) f(\vec{k} - \vec{q}) & \left(\sum_{\nu\sigma} e^{i(\vec{q}-\vec{s}) \cdot \vec{R}_{\nu}} e^{i\vec{q} \cdot \vec{R}_{\sigma}} \int \phi_n^*(\vec{s}, \vec{r}) [(\vec{r} + \vec{R}_{\nu}) \times \vec{p}] \phi_n(\vec{q}, \vec{r} - \vec{R}_{\sigma}) d^3r \right. \\ & \left. + \sum_{\nu\sigma} e^{i(\vec{q}-\vec{s}) \cdot \vec{R}_{\nu}} e^{-i\vec{s} \cdot \vec{R}_{\sigma}} \int \phi_n^*(\vec{s}, \vec{r} - \vec{R}_{\sigma}) [(\vec{r} + \vec{R}_{\nu}) \times \vec{p}] \phi_n(\vec{q}, \vec{r}) d^3r \right). \end{aligned} \quad (2.23)$$

To reduce this, we use the identities

$$\sum_{\nu} e^{i(\vec{q}-\vec{s}) \cdot \vec{R}_{\nu}} = \frac{(2\pi)^3}{\Omega} \delta(\vec{q} - \vec{s}), \quad (2.24)$$

$$\sum_{\nu} \vec{R}_{\nu} e^{i(\vec{q}-\vec{s}) \cdot \vec{R}_{\nu}} = -i \frac{(2\pi)^3}{\Omega} \nabla_{\vec{q}} \delta(\vec{q} - \vec{s}). \quad (2.25)$$

It is also convenient to define

$$\vec{p}_{mn}(\vec{s}, \vec{q}) = \sum_{\sigma} e^{-i\vec{s} \cdot \vec{R}_{\sigma}} \int d^3r \phi_m^*(\vec{s}, \vec{r} - \vec{R}_{\sigma}) \vec{p} \phi_n(\vec{q}, \vec{r}). \quad (2.26)$$

The usual momentum matrix $\vec{p}_{mn}(\vec{q})$ element is obtained when $\vec{s} = \vec{q}$. We will, however, require the more general object defined by (2.26). Finally, we introduce

$$\vec{I}_{mn}(\vec{q}) = \sum_{\sigma} e^{-i\vec{q} \cdot \vec{R}_{\sigma}} \int d^3r \phi_m^*(\vec{q}, \vec{r} - \vec{R}_{\sigma}) (\vec{r} \times \vec{p}) \phi_n(\vec{q}, \vec{r}). \quad (2.27)$$

Equation (2.23) can be simplified with the aid of (2.24)–(2.27),

$$\begin{aligned} L_n^{(1)}(\vec{k}) = \int d^3q f^2(\vec{k} - \vec{q}) & \times \{ \text{Re}[\vec{I}_{nn}(\vec{q})] + \text{Im}[\nabla_{\vec{s}} \times \vec{p}_{nn}(\vec{s}, \vec{q})]_{\vec{s}=\vec{q}} \} \\ & + \text{Im} \int d^3q f(\vec{k} - \vec{q}) [\nabla_{\vec{q}} f(\vec{k} - \vec{q})] \times \vec{p}_{nn}(\vec{q}, \vec{q}). \end{aligned} \quad (2.28)$$

In Eq. (2.28), Re and Im denote real and imaginary parts, respectively. It is now possible to allow f^2

to become a δ function. We also note that $p_{nn}(\vec{q}, \vec{q})$ is real. Equation (2.28) becomes

$$L_n^{(1)}(\vec{k}) = \text{Re}[L_{nn}(\vec{k})] + \text{Im}[\nabla_{\vec{s}} \times \vec{p}_{nn}(\vec{s}, \vec{k})]_{\vec{s}=\vec{k}}. \quad (2.29)$$

In order to investigate the last term in (2.29) in more detail, we substitute (2.22), and introduce the matrix elements of momentum between orbitals of the basis set \vec{p}'_{ij}

$$\vec{p}'_{ij}(\vec{k}) = \sum_{\sigma} e^{-i\vec{k} \cdot \vec{R}_{\sigma}} \int d^3r u_i^*(\vec{r} - \vec{R}_{\sigma}) \vec{p} u_j(\vec{r}) d^3r. \quad (2.30)$$

Thus, we have

$$\vec{p}_{nn}(\vec{s}, \vec{k}) = \sum_{ij} c_{ni}^*(\vec{s}) \vec{p}'_{ij}(\vec{s}) c_{nj}(\vec{k}). \quad (2.31)$$

We find

$$\text{Im} \lim_{\vec{s}=\vec{k}} [\nabla_{\vec{s}} \times \vec{p}_{nn}(\vec{s}, \vec{k})] = \text{Im} \left(\sum_{ij} c_{ni}^*(\vec{k}) \vec{p}'_{ij}(\vec{k}) \times \nabla_{\vec{k}} c_{nj}(\vec{k}) \right)$$

and

$$\begin{aligned} \vec{L}_n^{(1)}(\vec{k}) = \text{Re}[\vec{I}_{nn}(\vec{k})] - \text{Im}[\nabla_{\vec{s}} \times \vec{p}_{nn}(\vec{k}, \vec{s})]_{\vec{s}=\vec{k}} \\ = \text{Re}[\vec{I}_{nn}(\vec{k})] + \text{Im} \left(\sum_{ij} c_{ni}^*(\vec{k}) \vec{p}'_{ij}(\vec{k}) \times \nabla_{\vec{k}} c_{nj}(\vec{k}) \right). \end{aligned} \quad (2.32)$$

This is all that would be obtained for $\vec{L}_n(\vec{k})$ if the calculation were made in the symmetric gauge (2.8). However, the last term is sensitive to the phase of the Bloch functions. If we make a transformation of the eigenvectors

$$c_{nj}(\vec{k}) = e^{iW(\vec{k})} c'_{nj}(\vec{k}), \quad (2.33)$$

we find

$$\begin{aligned} \vec{L}_n^{(1)}(k) &= \vec{L}_n^{(1)'}(\vec{k}) \\ &+ \text{Im} \left(\sum_{ij} c_{ni}^*(\vec{k}) \vec{p}'_{ij}(\vec{k}) c_{nj}(\vec{k}) \times i \nabla_k W(\vec{k}) \right) \\ &= L_n^{(1)'}(\vec{k}) + \vec{p}_{nm}(k) \times \nabla_k W(\vec{k}), \end{aligned} \quad (2.34)$$

in which $L_n^{(1)'}$ has the same form in terms of the c' as $L_n^{(1)}$ did in terms of the c . This is, in principle, a serious difficulty since the relative phase of the eigenvectors c computed at neighboring points of the Brillouin zone may vary in an apparently random manner as a result of the computer program used to diagonalize the Hamiltonian matrix.

The second term on the right-hand side of (2.17) will be denoted $\vec{L}_n^{(2)}(\vec{k})$. It can be analyzed in the same way as $L_n^{(1)}$,

$$\begin{aligned} \vec{L}_n(k) &= \vec{L}_n^{(1)}(\vec{k}) - \vec{L}_n^{(2)}(\vec{k}), \\ \vec{L}_n^{(2)}(\vec{k}) &= \langle \eta \vec{k} | \vec{r} | \eta \vec{k} \rangle \times \langle \eta \vec{k} | \vec{p} | \eta \vec{k} \rangle \\ &= \left[\text{Re}[\vec{r}_{nn}(\vec{k})] - \text{Im} \left(\sum_{ij} c_{ni}^*(\vec{k}) I_{ij}(\vec{k}) \nabla_k c_{nj}(\vec{k}) \right) \right] \\ &\quad \times \vec{p}_{nn}(\vec{k}), \end{aligned} \quad (2.35)$$

in which $I_{ij}(\vec{k})$ is an element of the orbital-overlap matrix

$$I_{ij}(\vec{k}) = \sum_{\sigma} e^{-i\vec{k} \cdot \vec{R}_{\sigma}} \int d^3r u_i^*(\vec{r} - \vec{R}_{\sigma}) u_j(\vec{r}) \quad (2.36)$$

and \vec{r}_{nm} is the nonsingular part of the diagonal part of the coordinate matrix element

$$\vec{r}_{nn}(\vec{k}) = \sum_{\sigma} e^{-i\vec{k} \cdot \vec{R}_{\sigma}} \int d^3r \phi_n^*(\vec{k}, \vec{r} - \vec{R}_{\sigma}) \vec{r} \phi_n(\vec{k}, \vec{r}). \quad (2.37)$$

The change of phase [Eq. (2.33)] gives

$$\vec{L}_n^{(2)}(\vec{k}) = \vec{L}_n^{(2)'}(\vec{k}) - \nabla_k W(\vec{k}) \times \vec{p}_{nm}(\vec{k}), \quad (2.38)$$

in which $L_n^{(2)'}$ has the same form as $L_n^{(2)}$ except that it contains the c' , and we have used an identity expressing the normalization of the Bloch wave function

$$\sum_{ij} c_{ni}^*(\vec{k}) I_{ij}(\vec{k}) c_{nj}(\vec{k}) = 1. \quad (2.39)$$

Evidently, the phase-dependent terms in (2.34) and (2.38) cancel.

Now we consider the explicit spin-orbit contribution (2.18). The electric field \mathcal{E} is obtained from the crystal periodic energy function V , $e\mathcal{E} = \nabla V$. As in the previous case we separate $\vec{D}_n(\vec{k})$ into two parts: $\vec{D}_n^{(1)}(\vec{k})$ being the first term on the right-

hand side of (2.18),

$$\vec{D}_n^{(1)}(\vec{k}) = \langle \eta \vec{k} | \vec{r} \times (\vec{s} \times \nabla V) | \eta \vec{k} \rangle. \quad (2.40)$$

The decomposition of this term is quite similar to that of $\vec{L}_n^{(1)}(k)$, and need not be described in detail. We define two kinds of matrix elements:

$$\begin{aligned} \vec{\Delta}_{nm}(k) &= \sum_{\rho} e^{-i\vec{k} \cdot \vec{R}_{\rho}} \int \phi_n(\vec{k}, \vec{r} - \vec{R}_{\rho}) \\ &\quad \times [\vec{r} \times (\vec{s} \times \nabla V)] \phi_n(\vec{k}, \vec{r}) d^3r \end{aligned} \quad (2.41)$$

and [analogous to (2.26)]

$$\begin{aligned} \vec{d}_{mn}(\vec{q}, \vec{k}) &= \sum_{\sigma} e^{-i\vec{q} \cdot \vec{R}_{\sigma}} \\ &\quad \times \int \phi_m(\vec{q}, \vec{r} - \vec{R}_{\sigma}) (\vec{s} \times \nabla V) \phi_n(\vec{k}, \vec{r}) d^3r. \end{aligned} \quad (2.42)$$

The result is

$$\begin{aligned} \vec{D}_n^{(1)}(\vec{k}) &= \text{Re}[\vec{\Delta}_{nn}(\vec{k})] - \text{Im}[\nabla_s \times \vec{d}_{nn}(\vec{k}, \vec{s})]_{k=s} \\ &= \text{Re}[\vec{\Delta}_{nn}(\vec{k})] + \text{Im} \left(\sum_{ij} c_{ni}^*(\vec{k}) d'_{ij}(\vec{k}) \times \nabla c_{nj}(\vec{k}) \right), \end{aligned} \quad (2.43)$$

in which $d'_{ij}(\vec{k})$ is the orbital-matrix element

$$d'_{ij}(\vec{k}) = \sum_{\sigma} e^{-i\vec{k} \cdot \vec{R}_{\sigma}} \int u_i^*(\vec{r} - \vec{R}_{\sigma}) (\vec{s} \times \nabla V) u_j(\vec{r}) d^3r. \quad (2.44)$$

$\vec{D}_n^{(1)}$ has the same sensitivity to the phase of the Bloch functions as $L_n^{(1)}$ had. The counter term is

$$\begin{aligned} \vec{D}_n^{(2)}(\vec{k}) &= \left[\text{Re}[\vec{r}_{nn}(k)] \right. \\ &\quad \left. - \text{Im} \left(\sum_{ij} c_{ni}^*(\vec{k}) I_{ij}(\vec{k}) \nabla_k c_{nj}(\vec{k}) \right) \right] \times \vec{d}_{nn}(\vec{k}), \end{aligned} \quad (2.45)$$

and the combination

$$\vec{D}_n(\vec{k}) = \vec{D}_n^{(1)}(\vec{k}) - \vec{D}_n^{(2)}(\vec{k}) \quad (2.46)$$

is unchanged by the change of phase (2.33).

There is one more term which must be analyzed in the same way. This is $\vec{Q}_n^{(2)}$, Eq. (2.20). However, this is a relativistic correction to a term L_n , which is already small: the ratio of $|\vec{Q}_n^{(2)}|/2m^2c^2$ to $|L_n|$ should be of the order of the ratio of the kinetic energy of a d electron to its rest energy. The former is of the order 15 Ry, so the ratio is about 4×10^{-4} . This we will ignore. A similar argument can be applied to $\vec{Q}_n^{(1)}$. The ratio $|\vec{Q}_n^{(1)}|/2mc^2|s_n|$ should be of this order as well. In transition metals (though not necessarily in alkali metals¹³) this is a correction smaller by

a factor of about 100 than \tilde{L}_n . We are unable to compute \tilde{L}_n to 1% accuracy, as is discussed in Sec. III, and so we will discard $\tilde{Q}^{(1)}$ as well as $\tilde{Q}^{(2)}$.

For completeness, we note that the spin moment term \tilde{S}_n can be expressed as

$$\tilde{S}_n(\vec{k}) = \sum_p e^{-i\vec{k}\cdot\vec{R}_p} \int \phi_n^*(\vec{k}, \vec{r} - \vec{R}_p) \vec{s} \phi_n(\vec{k}, \vec{r}) d^3r. \quad (2.47)$$

The procedures and results of our numerical calculations are summarized in Sec. III.

III. COMPUTATIONS AND RESULTS

The computation of the g factor utilized the wave functions and energy levels obtained in previous calculations.^{18,19} The basis set employed consisted of 38 terms for each spin (\uparrow , \downarrow), as follows. Atomic wave functions expressed as linear combinations of Gaussian-type orbitals as determined by a self-consistent calculation of Wachters²⁰ were employed for all states except $3d$ ($1s, 2s, 3s, 4s, 2p, 3p, 4p$). Five independent Gaussian-type orbitals were introduced for each of the five $l=2$ angular functions. The orbital exponents used in defining these functions were the same as employed by Wachters. Exchange was included in the spin polarized $X\alpha$ approximation²¹ (with $\alpha = \frac{2}{3}$ for nickel²² and $\alpha = 0.64$ for iron). The calculations were iterated, neglecting spin-orbit coupling, until self-consistency was achieved. The spin-orbit interaction was then inserted, and a final set of energy bands was obtained. The direction of spin alignment was chosen as $(0, 0, 1)$, and is called z . Additional details can be found in the references cited.^{18,19}

The computation of the elements $\tilde{I}_{mn}(\vec{k})$ is quite simple and straightforward. Equation (2.22) is inserted into (2.27) which becomes

$$I_{mn}^{(z)}(\vec{k}) = \sum c_{ni}^*(\vec{k}) c_{nj}(\vec{k}) \times \left(\sum_{\sigma} e^{-i\vec{k}\cdot\vec{R}_{\sigma}} \int u_i^*(\vec{r} - \vec{R}_{\sigma}) l_z u_j(\vec{r}) d^3r \right) \quad (3.1)$$

The operator l_z in (3.1) affects only the angular part of the function u_j . The orbital matrix element is proportional to an element of the overlap matrix, and the evaluation of $I_{mn}^z(\vec{k})$ requires little more than a rearrangement of the overlap matrix. If spin orbit coupling is neglected, the sum of (3.1) over equivalent \vec{k} in a star is zero; however, the inclusion of spin-orbit coupling modifies the wave functions of the Bloch states so that a non-vanishing result is obtained. Apart from the spin

moment $S_n^{(z)}$ this term gives the largest contribution to \tilde{M} . The numerical evaluation of (3.1) included 1357 points in $\frac{1}{16}$ th of the Brillouin zone for nickel and 729 points for iron. The sum included all orbitals in the basis set and was carried to convergence in regard to the direct lattice sum. The contribution to M from this term, summed over all occupied states is 0.0448 for nickel and 0.0588 for iron.

In contrast, the derivative terms in $L_n^{(1)}$, Eq. (2.32), are extremely difficult to evaluate. The orbital matrix elements $\tilde{p}'_{ij}(k)$, Eq. (2.30), can be made real by a unitary transformation. In the absence of spin-orbit coupling, the same transformation makes the Hamiltonian into a real matrix, and consequently the coefficients c_{ni} are real. Hence these terms vanish for zero spin-orbit coupling. The inclusion of spin-orbit coupling leads to a complex (but Hermitian) Hamiltonian and then to complex coefficients c_{ni} , so that the derivative terms are no longer zero. We have attempted to estimate the derivative contribution to Eq. (2.32) by approximate numerical differentiation of the wave function expansion coefficients c_{ni} on a mesh of points in $\frac{1}{16}$ th of the Brillouin zone. This calculation is rather crude, and is subject to difficulties in the vicinity of points where there is an avoided crossing of the bands. Details of the estimation procedure can be found in Ref. 23. We find that this term is about 5% or less of the main (\tilde{I}_{mn}) term in both iron and nickel. The quantity $L_n^{(2)}$, Eq. (2.35), has also been estimated for nickel. We found $L_n^{(2)} = -7.6 \times 10^{-4}$, about 2% of the dominant term. However, we do not believe that we have been able to obtain accurate numerical values for terms involving derivatives and are therefore neglecting both the derivative terms in (2.32) and (2.35) in quoting our final results for $\langle M \rangle$. This is the main limitation of our numerical work.

The spin-orbit term $\Delta_n^{(z)}(\vec{k})$ [Eq. (2.41)] can be calculated in a straightforward way. In this case, it is sufficiently accurate to neglect overlap, and include only the contribution in which the wave functions and potentials are centered on the same site. Numerical evaluation gave a contribution 0.0003 in atomic units for iron. This is negligible, and, in view of the small value obtained for iron, a numerical calculation for nickel was not performed. For the same reason, the derivative terms in (2.43) and $D_n^{(2)}$, Eq. (2.45), were neglected. Retention of the terms discarded here may be more important in systems, like the alkali metals, where the dominance of $l_{mn}(\vec{k})$ is less pronounced.

We can now compute g and g' from (1.1), using the spin moments of $0.62\mu_B$ (Ni) and $2.29\mu_B$ (Fe) also obtained from the band calculation. The results are

	$g(\text{th})$	$g'(\text{th})$	$g(\text{expt})$	$g'(\text{expt})$
Fe	2.05	1.95	2.09	1.919
Ni	2.14	1.87	2.18	1.835

The experimental values for Ni are taken from Ref. 6 and those for Fe from Refs. 7 and 9. If we use the experimental magneton numbers (2.12 for Fe, 0.56 for Ni) instead of those coming from the band calculation, the predicted values of g and g' are changed slightly, becoming 2.06 and 1.95 for Fe, respectively, and 2.16 and 1.86 for Ni.

Our result for g' in nickel agrees reasonably well with that calculated by Arlinghaus and Reck⁴ who obtained $g' = 1.86$. Their computation was based on a semiempirical band-structure calculation by Ehrenreich and Hodges,²⁴ and neglected

overlap and hybridization contributions to $\vec{I}_{nn'}(\vec{k})$. Arlinghaus and Reck did not attempt to estimate corrections due to the other contributions to \vec{M} described here.

The agreement between theoretical and experimental results is moderately good for nickel but somewhat poorer for iron. We have no explanation for the discrepancies, since it seems quite unlikely that the major uncertainty in the present calculations; the contribution of the derivative terms to $\vec{L}_n(\vec{k})$, could be large enough to increase \vec{M} by the percentage required.

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